SCIENCE FOR GLASS PRODUCTION

UDC 666.11.01

GLASS WITH MODIFIED TITANIUM COATINGS

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Translated from *Steklo i Keramika*, No. 11, pp. 3 – 4, November, 2008.

The results of investigations of glasses with modified titanium coatings are presented. It is found that appropriate treatment if glasses with coatings containing titanium nitride can give a modified titanium dioxide layer which exhibits photocatalytic activity. It is shown there is promise in developing photocatalytically active glasses by thermal modification of reflective coatings which are obtained by vacuum technology and whose outer layer contains titanium.

Contemporary trends in architecture and construction are dictating new requirements, such as heat-insulation, conditioning, aesthetic appeal, and so on, for light-transmitting elements. Modification of sheet-glass surfaces by means of films consisting of metal compounds (including Sn, Fe, Ti, Ag, and others) has made it possible to obtain glass with a complex of unique properties [1].

Films with titanium derivatives (oxides, nitrides) possess high reflectivity in the region of the solar spectrum and impart to glass color and specularity whose degree is regulated by the number, deposition sequence, and thickness of the layers. Glasses coated with titanium nitride films are obtained by vacuum methods in single- and multilayer variants. Large-format glass coated with films based on titanium dioxide is produced primarily by pyrolytic methods, since the coating deposition rate in vacuum methods is low. Titanium-containing films belong to the class of reflective coatings. Glass with such films gives protection against sunlight and is used effectively for fenestration of administrative and public buildings, where the area of photo-transparent structures reaches 100% of the area of the façade. Obviously, the profitability and aesthetic appeal of such buildings depend greatly on the cost of keeping the windows clean. The need to reduce expenditures for such purposes to a minimum has dictated new requirements for construction glass — a self-cleaning capability.

The surface of the coating must possess two basic properties which make the glass self-cleaning. These properties have been termed photocatalytic and ultraviolet effects. In the first place, a chemical reaction decomposes organic compounds on a glass surface under the action of ultraviolet light and oxygen. In the second place, water does not collect in drops but rather drips down along the glass forming a thin film. It wets the dirt, washes it off, and then rapidly dries without leaving streaks [2, 3].

The investigations performed at the Pilkington Company (Great Britain) have shown that titanium dioxide films exhibit a photocatalytic effect and can decompose dirt on glass surfaces. In 2000 this company developed and produced for studying the demand a self-cleaning glass with a TiO_2 film under the trade name “Pilkington-Active.” This glass is now produced in the USA, Japan, Europe, and the Commonwealth of Independent States using modern technologies [4].

Self-cleaning glasses coated with TiO_2 have high light transmission. The films are 50 nm and more thick. As the thickness of the TiO_2 coating increases, the glass acquires solar protective properties with reflection coefficient up to 29% in the visible range of the spectrum [5].

The photocatalytic activity of TiO_2 films is due to photoelectric generation of electron – hole pairs in the semiconductor film coating under solar illumination. In moist air, moisture decomposes on them and hydroxy- and pyroxy-radicals are produced and active oxygen is released. The latter is a strong oxidizer and decomposes organic dirt on glass surfaces (RF Patent No. 2269495).

In the course of the investigations on heat-treatment hardening and quenching of reflective glass with titanium nitride film coatings, we obtained samples with higher light transmission and reflection coefficients and mechanical durability [6].

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It was determined that modification of the properties of reflective coatings is due to the partial or complete oxidation of titanium nitride with formation of oxides. It is of definite interest to study the possibility of fabricating TiO_2-based photocatalytically active glass obtained during heat-treatment hardening of reflective glass with film coatings based on titanium derivatives.

It is known that self-cleaning titanium dioxide coatings are obtained by the pyrolytic method at temperatures 560 – 650°C. Consequently, the experimental samples were heat-treated at 600°C [5].

The photocatalytic activity was determined using a procedure (RF Patent No. 2269495) in which the presence of the catalytic activity was determined microscopically according to its vanishing under exposure of samples on which a stearic acid film was deposited before exposure to sunlight. The duration of the experiment was 38 days. The air temperature was about 30°C.

Photocatalysis is a complex multifactor process occurring on the surface. The intensity of this process is affected by the presence of catalytically active impurities, the heterogeneous structure in multilayer coatings, and so on.

The presence of catalytic activity was investigated on glass samples with a multilayer coating obtained by vacuum magnetron sputtering in a dc regime in a medium consisting of a mixture of argon and nitrogen gases.

The samples were heat-treated at 600°C in a heated furnace at the Tamglass Company (Finland) in a regime for strengthening 4-mm thick glass.

A Philips XL 30 ESEM scanning electron microscope with an EDAL Pegasus attachment for local x-ray microanalysis was used to analyze the surface of the initial and heat-treated samples of glass with a multilayer coating. It was determined that during the heat-treatment of such glass the glass density increases. Quenching the glass decreases the thickness of the coating. The surface layer of the glass contains TiO_2 and an elevated content of sodium and iron nitrides is observed.

The corrosion resistance was investigated in a G-4 hydrostat in a regime with heating and cooling in the temperature range 20 – 70°C for 40 days. It was found that glass acquires high adhesion and corrosion resistance during quenching.

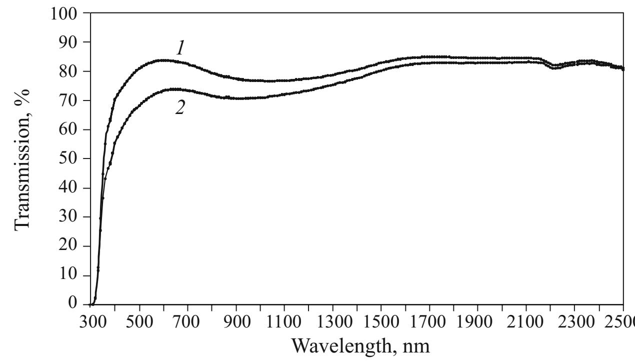

Fig. 1. Transmission spectra of Pilkington-Active self-cleaning glass (*1*) and experimental heat-treatment hardened glass (*2*).

Microanalysis showed no micro-separations on heat-treatment hardened samples. The results of the tests for corrosion resistance of the initial (uncoated) glass and coated glass are presented in Table 1.

Microscopic investigations of the experimental samples with a heat-treatment hardened coating, which were performed with a MIN-8 polarization microscope, showed the presence of a photocatalytic effect.

A durability study which we performed previously of the influence of heat-treatment hardening of glass showed that heat-treatment hardened samples have a higher durability [6].

A Lambda-950 spectrophotometer was used to perform comparative IR-spectroscopic studies of the Pilkington-Active self-cleaning glass and the heat-treatment hardened sample in the visible and solar IR ranges. The results obtained are displayed in Fig. 1. The spectral transmission curves of the experimental samples are practically identical.

In summary, a modified, photocatalytically active layer of titanium dioxide can be obtained by heat-treatment of glass with coatings containing titanium nitride. Glass with heat-treatment hardened coatings has high corrosion resistance and durability.

The experimental data showed that there is promise in developing photocatalytically active glass by thermal modification of reflective coatings with titanium-containing outer layer, which are obtained by a vacuum technology.

TABLE 1.

Glass	Form of the glass surface* after, days											
	2	6	8	12	16	20	23	26	29	33	35	40
Initial (uncoated)	Cl	Cl	Cl	Cr	Cr	Cr	Cr	Cr	Not determined			
Coated	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cr	Cr	Not determined
With heat-treatment hardened coating	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl

* Cl) clean surface; Cr) corrosion of the coating (point corrosion).

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